Bacteriogenic Origin of Secondary Minerals in Ohio Based on Carbon and Sulfur Isotope Compositions

A Senior Honors Thesis

Presented in partial fulfillment of the requirements for graduation with distinction in Geological Sciences in the undergraduate colleges of The Ohio State University

by

Theresa M. Baiamonte

The Ohio State University
June 1998

Approved by:

Dr. Gunter Faure

Bacteriogenic Origin of Secondary Minerals in Ohio Based on Carbon and Sulfur Isotope Compositions

Theresa M. Baiamonte
Dr. Gunter Faure, adviser
Department of Geological Sciences

Abstract

The origin of secondary minerals in northwestern Ohio has been attributed to a variety of causes including magmatic and bacterial activity. This research was conducted to determine whether secondary calcite, pyrite, sphalerite, galena, and celestite in Ohio result from bacterial processes. This combination of minerals is similar to those of Mississippi Valley type deposits, which have yielded economic wealth in other areas.

The carbon isotope composition in secondary calcite establishes a link with petroleum by exhibiting $\delta^{13}C$ values of -21.5‰ to -27.6‰. The $\delta^{34}S$ values of sulfide minerals (-24.2‰ to +7.0‰) demonstrate consistent depletion in the heavy sulfur isotope compared to coexisting sulfate minerals whose $\delta^{34}S$ values range from +28.4‰ to +66.4‰. The isotope fractionation of carbon and sulfur minerals confirms that sulfur-reducing bacteria metabolized hydrocarbons by means of oxygen derived by reduction of sulfate to sulfide. The CO_2 and H_2S released by bacteria resulted in the deposition of secondary carbonate and sulfide minerals in the rocks of northwestern Ohio.

Introduction

Minerals such as calcite ($CaCO_3$), pyrite (FeS_2), sphalerite (ZnS), galena (PbS) and celestite ($SrSO_4$) occur in dolomites and limestone in northwestern Ohio and southern Michigan. Sphalerite and galena are ore minerals of zinc and lead, respectively, and therefore have commercial value.

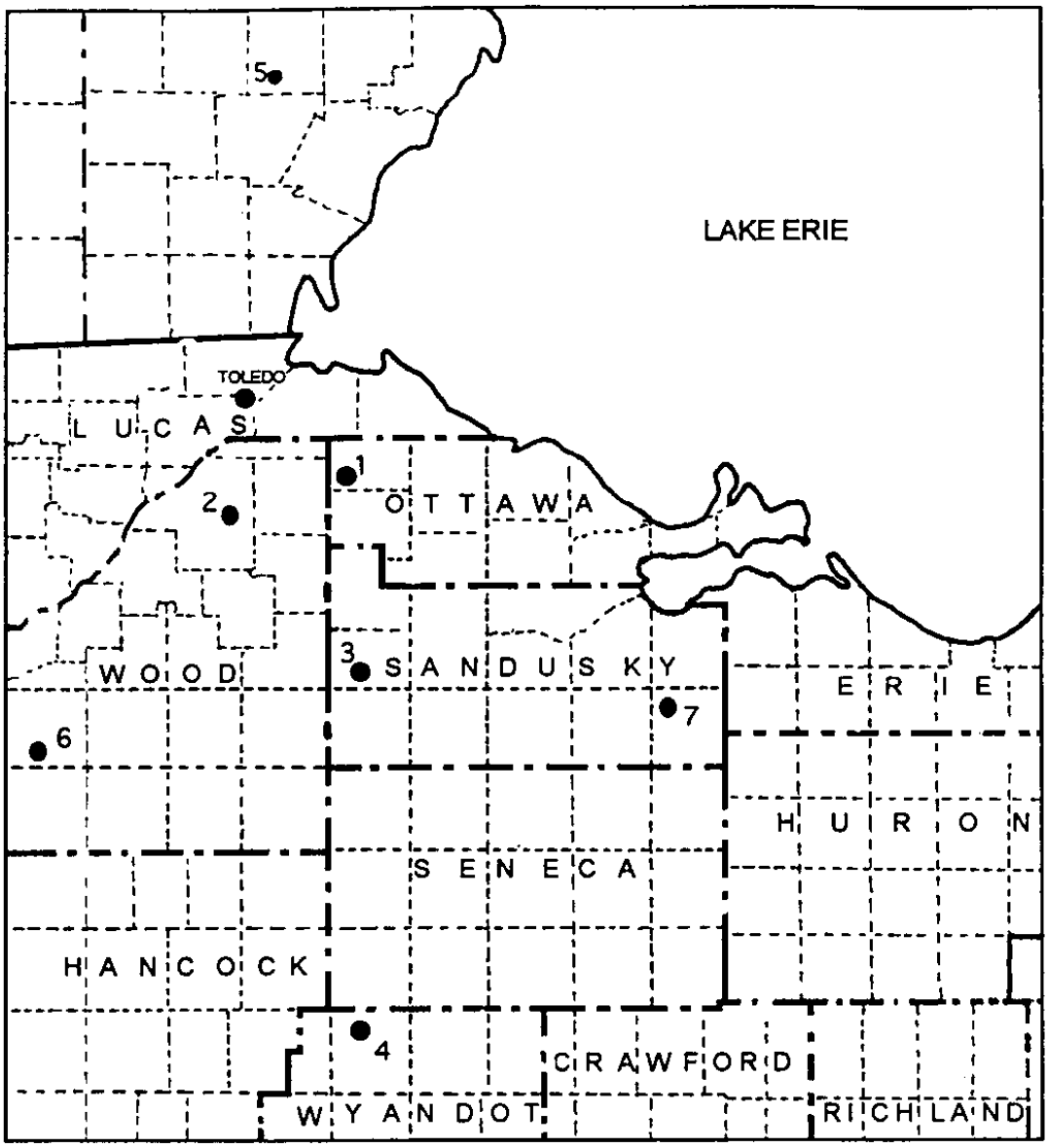
Secondary minerals form after the deposition of dolomite or limestone. The minerals may occur in fractures, solution cavities, or other structural features that occur after the deposition of the original host rock. The origin of these minerals has been a topic of discussion for many years. Botoman and Faure (1976) suggested a magmatic origin for some locations and the activity of bacteria for others. Haden (1977) also mentioned bacteria as a possible factor in the deposition of secondary minerals. However, there were not sufficient amounts of isotope analyses to make this determination.

The object of this study was to test the hypothesis that secondary minerals in northern Ohio are the result of bacterial processes. If this is the case, the isotope composition of sulfide minerals should differ from that of coexisting sulfate minerals, whereas the isotope composition of carbon in secondary calcite should approach that of coexisting petroleum or natural gas.

Geology of Northwestern Ohio and Southern Michigan

The study area includes parts of northwestern Ohio and southern Michigan in Figure 1. This area is underlain by carbonate rocks of Silurian and Devonian age. Silurian formations in this area include (from oldest to youngest) the Lockport Dolomite (with the Guelph Dolomite as its upper layer)(Janssens, 1977), the Greenfield Dolomite and the Tymochtee Dolomite of the Salina Group (Carlson, 1991), and the Raisin River Dolomite (Janssens, 1968), also known as the Bass Islands Dolomite (Carlson, 1991). There is an unconformity between the Silurian and Devonian systems (Janssens, 1970) because rock layers of Early Devonian age were removed by erosion. The Middle Devonian rocks are represented (from oldest to youngest) by the Detroit River Group, followed by the Dundee Limestone, the Traverse Group, and the Ohio Shale (Janssens, 1970) (Figure 2).

Structural features of this area include the Findlay Arch, which formed after the Silurian period (Janssens, 1977). It caused the strata in the western part of the study



Main Study Area

Figure 1 Map of northwestern Ohio and southern Michigan showing quarry locations, numbered corresponding to Table 1. Quarries at Clay Center (1), Lime City (2), Gibsonburg (3), Findlay (4), Maybee (5), Custar (6), and Sandusky Co. (7) are identified on the map of the Main Study Area. The state map of Ohio shows the location of the petroleum sample from Pickaway Co. (8). This figure was adapted from a map by the Ohio Geological Survey.

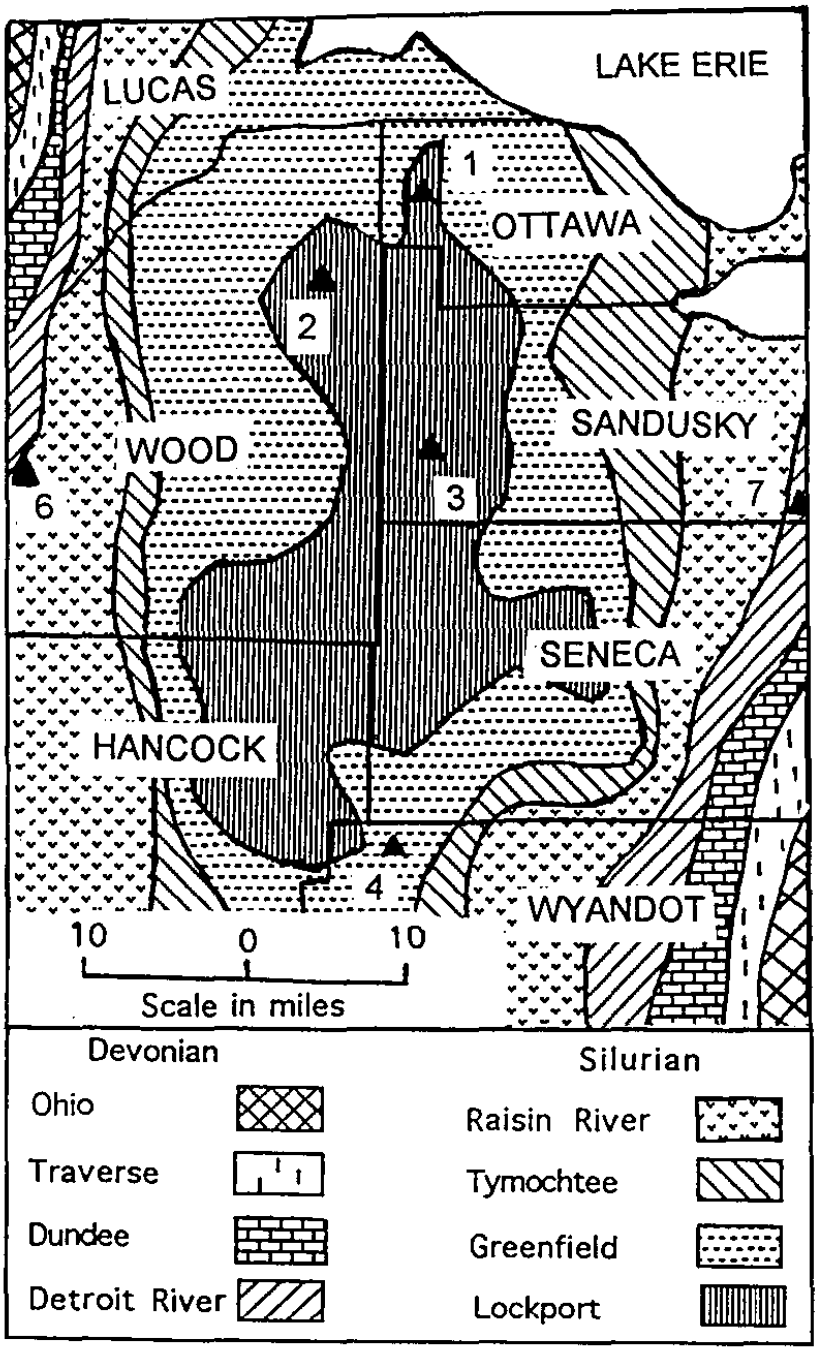


Figure 2 General geology of northwest Ohio. Quarry locations are numbered corresponding to Table 1. Quarries at Clay Center (1), Lime City (2), Gibsonburg (3), Findlay (4), Custar (6), and Sandusky Co. (7) are identified on this map. This figure was adapted from Botoman and Faure (1976).

area to dip to the west, and the strata in the eastern part to dip to the east. The locations and geology of the collecting sites are described in Table 1.

Mississippi Valley Type Deposits

Mississippi Valley type deposits (MVT) have been a source of lead and zinc in Europe and North America. The deposits in the United States occur primarily in the Tri-State district of Oklahoma-Kansas-Missouri, but have also been productive in Kentucky, Tennessee, and Illinois. (Guilbert and Park, 1986)

Mississippi Valley type deposits (MVT) are characterized by dolomites containing galena, sphalerite, barite, and fluorite in significant quantities with accessory pyrite and marcasite (Guilbert and Park, 1986). The suite of minerals collected from the quarries in northwest Ohio fit into this categorization as suggested by Haden (1977) and Botoman and Stieglitz (1978).

Additional support for the link between Ohio and MVT deposits is the lack of nearby bodies of igneous rock, the gentle dips of the rocks, the low temperatures of deposition (e.g. 50-225°C) (Guilbert and Park, 1986). Botoman and Faure (1976) reported temperatures of 43-63°C for sulfide minerals in Ohio based on sulfur isotope compositions of coexisitng sphalerite and galena. This temperature range is consistent with that of MVT deposits.

Theories of Ore Deposition

The deposition of the secondary minerals in the rocks of Ohio is attributable to a range of possibilities including syngenic deposition with the carbonate host rocks. This explanation is unlikely in this case because the mineralization occurs in fractures and cavities that formed after deposition of the rocks. The minerals could have been deposited by hydrothermal fluids of igneous derivation (Guilbert and Park, 1986). However, there is

Table 1 Northwestern Ohio and southern Michigan quarry locations and geology. The site numbers correspond to the numbers shown on Figures 1 and 2. Data from Haden (1977) and Botoman and Faure (1976) have also been included.

Site Number	Locality	Host Rock	Minerals
1	Edward Kramer and Sons, Inc., Clay Center, Allen Twp., Ottawa County, Ohio	Dolomite Middle Silurian Lockport Group	Calcite, Galena, Sphalerite, Pyrite, Celestite
2	France Stone Co. Quarry, Lime City, Perrysburg Twp., Wood County, Ohio	Dolomite Middle Silurian Lockport Group	Calcite, Galena, Sphalerite, Marcasite, Celestite, Native Sulfur
3	Charles Pfizer and Co., Gibsonburg, Madison Twp., Sandusky County, Ohio	Dolomite Middle Silurian Lockport Group	Galena, Sphalerite, Fluorite
4	National Lime and Stone Co., Findlay, Crawford Twp., Wyandot County, Ohio	Dolomite Upper Silurian Greenfield	Celestite
5	Maybee Quarry, Maybee, Monroe County, Michigan	Dolomite Middle Devonian Detroit River Group	Calcite, Celestite, Native Sulfur
6	Pugh Quarry Co., Custar, Milton Twp., Wood County, Ohio	Dolomite Middle Devonian Detroit River Group	Calcite, Celestite, Native Sulfur
7	France Stone Quarry, York Twp., Sandusky County, Ohio	Dolomite Middle Devonian Detroit River Group	Calcite, Fluorite
8	Pickaway County, Ohio	Dolomite Middle Devonian Beekmantown Dolomite	Petroleum

no evidence of igneous activity in northwestern Ohio. A third possibility is that the minerals were deposited by hot brines. Heyl et al. (1973) reported that the lead in some Mississippi Valley deposits had originated from the underlying basement rocks as indicated by the isotope compositions of lead and sulfur. Such brines may arise by the following steps outlined by Spencer (1987):

1. Formation of marine basins that became isolated from the open ocean
2. Evaporative concentration and formation of evaporite minerals
3. Downward migration of dense brines
4. Heating by geothermal gradient
5. Possible compositional modification of brines by reactions with basement rocks
6. Ascent of hot brines along faults or other conduits
7. Trapping of brines in reservoir rocks such as layers of porous dolomite

The association of sulfate-rich brines with hydrocarbons in the same reservoir permits sulfur-reducing bacteria to metabolize hydrocarbons by means of oxygen derived by reduction of the sulfate ions to sulfide ions. Sulfur-reducing bacteria are widely dispersed on the Earth today and have existed throughout most of geologic time. *Desulfovibrio desulfuricans* is the most common of these, but *Desulfovibrio orientis* is another species that also might favor this habitat (Guilbert and Park, 1986). The bacteria derive energy from petroleum and break the S-O bond of the sulfate in order to recover the oxygen. This process can be described using the approximation by Davis and Kirkland (1970):

$$\text{Bacteria} + \text{Petroleum Hydrocarbons} + \text{Sulfate} = CO_2 + H_2S + \text{Energy} \qquad (1)$$

The bacteria release H_2S which is enriched in the lighter sulfur isotope (^{32}S) because the ^{32}S-O bond is weaker than the ^{34}S-O bond. Pure cultures of sulfate-reducing bacteria have produced sulfide depleted in ^{34}S by 4 to 46‰ (Hoefs, 1997). The H_2S gas may then react with metal ions to form sulfide minerals (Guilbert and Park, 1986). For this reason, the sulfur in secondary minerals such as sphalerite and galena is enriched in ^{32}S (depleted in ^{34}S) compared to the remaining sulfate. Additionally, the carbon dioxide can react to form calcite ($CaCO_3$), which means the isotope composition of carbon in the secondary calcite should be negative because the petroleum has a negative $\delta^{13}C$ (generally around -28‰) (Faure, 1986).

Isotope Geochemistry of Carbon and Sulfur

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. They are represented by using the notation ^{m}E, where E is the symbol for the element (such as S for sulfur) and m is the mass number (i.e. sum of the number of protons and neutrons in the nucleus). It is common to express isotopic composition in terms of "delta" (δ) values, in which a sample (carbon is used as an example) is compared to a standard in the equation:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \times 1000 \qquad (2)$$

The resulting number is expressed in ‰. A positive $\delta^{13}C$ value indicates that the sample is more enriched in ^{13}C (or more depleted in ^{12}C) than the standard. Likewise, a negative $\delta^{13}C$ value indicates the sample is more depleted ^{13}C (or more enriched in ^{12}C) than the standard.

The carbon isotope standard is the belemnite *Belemnitella americana* from the Peedee Formation in South Carolina, also called PDB. Dolomites of marine origin can be expected to have $\delta^{13}C$ values around zero, because the dolomite is being compared to a standard also of marine origin. Photosynthesis concentrates ^{12}C in plant tissue so that organic matter in sediment may have $\delta^{13}C$ ranging from -10 to -30‰, reflecting an enrichment in ^{12}C (or depletion in ^{13}C).

The sulfur isotope standard is the mineral troilite (FeS) from the Canyon Diablo meteorite. This is an appropriate standard because the isotopic composition of sulfur in mafic igneous rocks is very similar to that of meteorites. Consequently, the $\delta^{34}S$ of a terrestrial sulfur sample can be used as a measure of the change that has occurred in its isotopic composition since its initial introduction into the crust of the Earth (Faure, 1986). Sulfur that has originated from a magmatic source can therefore be expected to have a $\delta^{34}S$ of around zero. In addition, sulfur has been recycled in the Earth's environment so that the combined action of bacteria and deposition of minerals causes sulfate deposited with marine carbonates to vary over time, ranging from +11 to + 34‰ (Faure, 1991).

Methods

The minerals from northwestern Ohio were obtained from a collection gathered by numerous people and stored in the Department of Geological Sciences at The Ohio State University. The petroleum sample is from central Ohio but should be applicable to northwestern Ohio because the $\delta^{13}C$ values for petroleum do not vary much. The samples were analyzed by Geochron Laboratories, Inc. using mass spectrometry to determine the values for $\delta^{13}C$ and $\delta^{34}S$. The isotope values obtained are listed in Table 2, along with data from Haden (1977) and Botoman and Faure (1976).

Table 2 Carbon and sulfur isotope data (in ‰) of minerals in quarries in northwestern Ohio and southern Michigan. The * signifies duplicate analyses of the same sample. Data were also used from Haden (1977) and Botoman and Faure (1976), signified by (a) and (b), respectively.

Location	Dolomite ($\delta^{13}C$)	Limestone ($\delta^{13}C$)	Calcite ($\delta^{13}C$)	Petroleum ($\delta^{13}C$)	Galena ($\delta^{34}S$)	Sphalerite ($\delta^{34}S$)	Pyrite ($\delta^{34}S$)	Celestite ($\delta^{34}S$)	Native Sulfur ($\delta^{34}S$)
Clay Center, OH	+1.0(a)		-11.0, -11.7(a)		-1.4, -1.1*	+ 1.4	+7.0(b)	+29.0(a)	
Lime City, OH	+2.3(a)		-21.5, -18.6(a)		-3.4(a)	-0.9(a)	-24.2(a)	+29.0, +28.4(a)	+14.2(a)
Gibsonburg, OH					-2.2(b)	+4.8(b)			
Findlay, OH								+ 32.4	
Maybee, MI	+ 0.6		-21.1(a)					+ 66.4	+ 13.3
Custar, OH							-21.9, -15.4(b)		
Sandusky Co., O	-9.3(a)	+1.0(a)							
Pickaway Co., OH				-27.5, -27.7*					

Results

Carbonates and Petroleum

The $\delta^{13}C$ values of dolomite from Clay Center, Lime City, and Maybee range from +0.6 to +2.3‰ (Table 2) and one sample of limestone from Sandusky, OH has a $\delta^{13}C$ value of +1.0‰. These values were expected since the limestone and dolomite are of marine origin and therefore should be similar to the standard. However, dolomite from Sandusky, OH had a $\delta^{13}C$ value of -9.3‰, which differs from the other dolomites. The $\delta^{13}C$ values of calcite are negative, from -21.5 to -11.0‰. Figure 3 depicts the $\delta^{13}C$ values for minerals at Clay Center, Lime City, Maybee and Sandusky. The isotopic composition of secondary calcite is intermediate between that of dolomite and petroleum, as illustrated in Figure 4. The average $\delta^{13}C$ value for dolomite and limestone is -1.3‰ and the average calcite $\delta^{13}C$ value is -16.78‰. The average calcite $\delta^{13}C$ is intermediate between the $\delta^{13}C$ values of the dolomite and the petroleum whose $\delta^{13}C$ is -27.6‰.

Sulfides, Native Sulfur and Sulfate

The sulfide $\delta^{34}S$ of galena and sphalerite cluster around zero, from -3.4 to +4.8‰, whereas the pyrite $\delta^{34}S$ values vary widely from -24.2 to +7.0‰. Celestite values all are positive (reflecting depletion of ^{32}S) and range from +28.4 to +66.4‰. Native sulfur values are +13.3‰ and +14.2‰. Figure 5 depicts the $\delta^{34}S$ values for minerals at Clay Center, Lime City, and Maybee. The average $\delta^{34}S$ for galena is -2.3‰ and the averages for sphalerite, pyrite, celestite, and native sulfur are (respectively) +1.76, -13.6, +39.2, and +13.75‰. The sulfide minerals all are depleted in ^{34}S compared to coexisting sulfate, as shown in Figure 6.

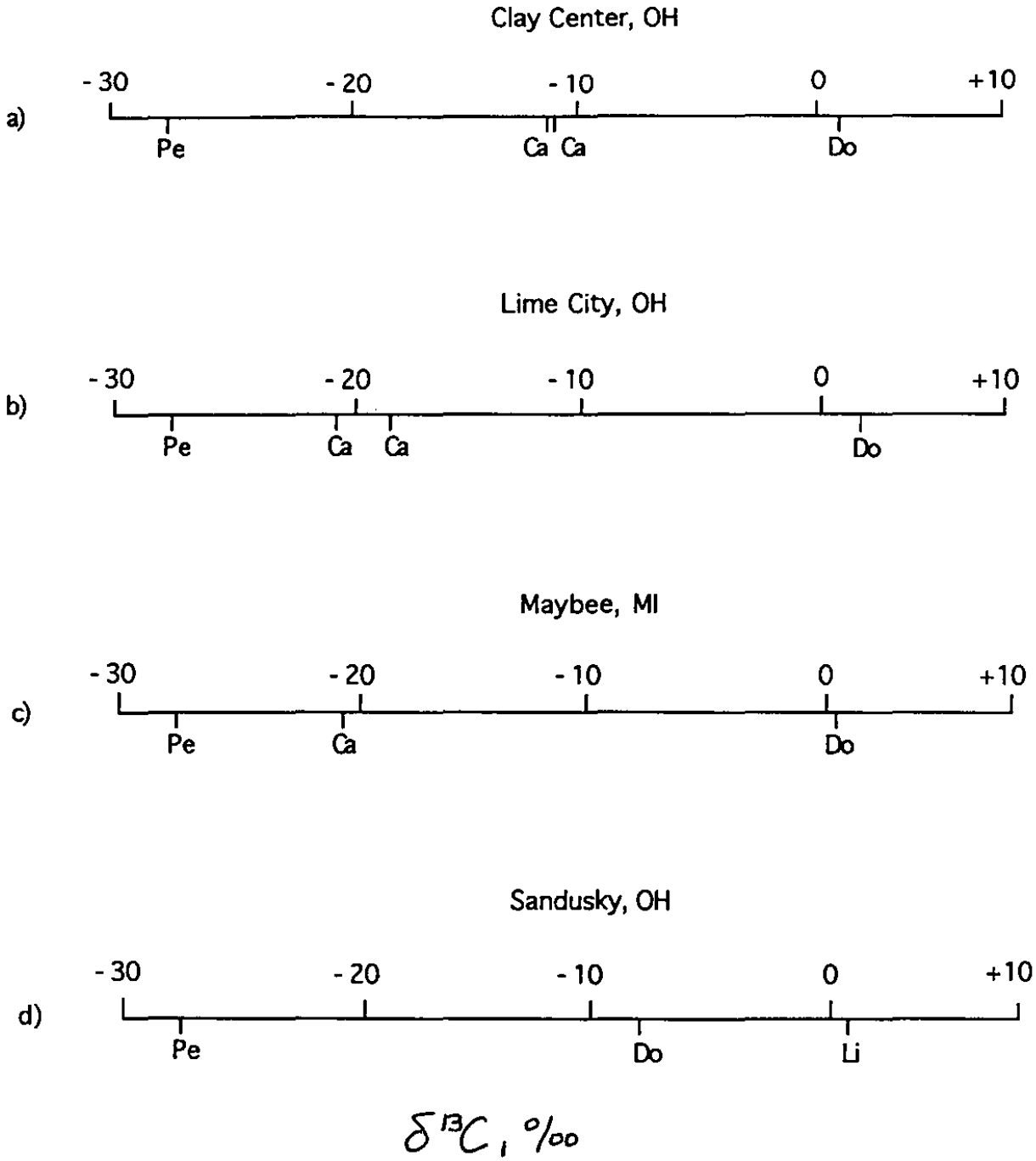


Figure 3 Carbon isotope compositions for the quarries at a) Clay Center, b) Lime City, c) Maybee, and d) Sandusky. The numbers refer to $d^{13}C$ (in ‰) and the letters Pe, Ca, Do and Li represent petroleum, calcite, dolomite and limestone, respectively. They are placed at the corresponding $d^{13}C$ on the scale. Notice that the $d^{13}C$ of calcite are located between petroleum and dolomite at Clay Center, Lime City, and Maybee.

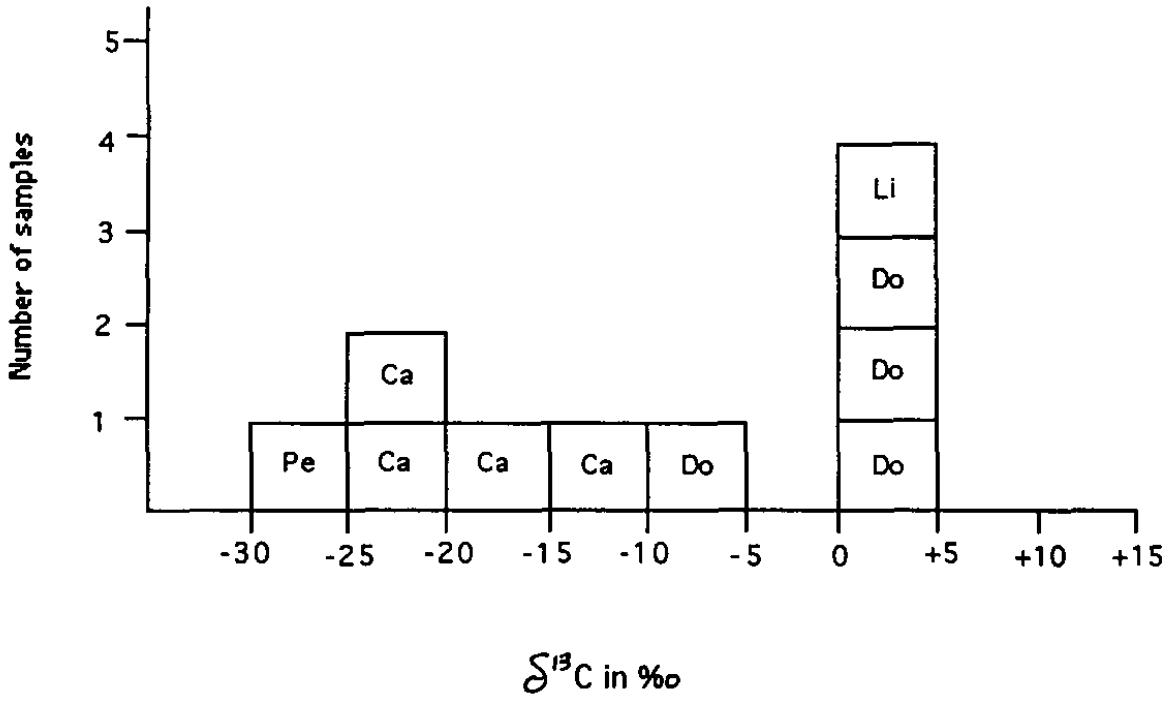


Figure 4 Histogram of $\delta^{13}C$ values for samples from northwestern Ohio and southern Michigan. The letters Pe, Ca, Do, and Li refer to petroleum, secondary calcite, dolomite, and limestone, respectively. Notice the calcite $\delta^{13}C$ values are located between petroleum and dolomite.

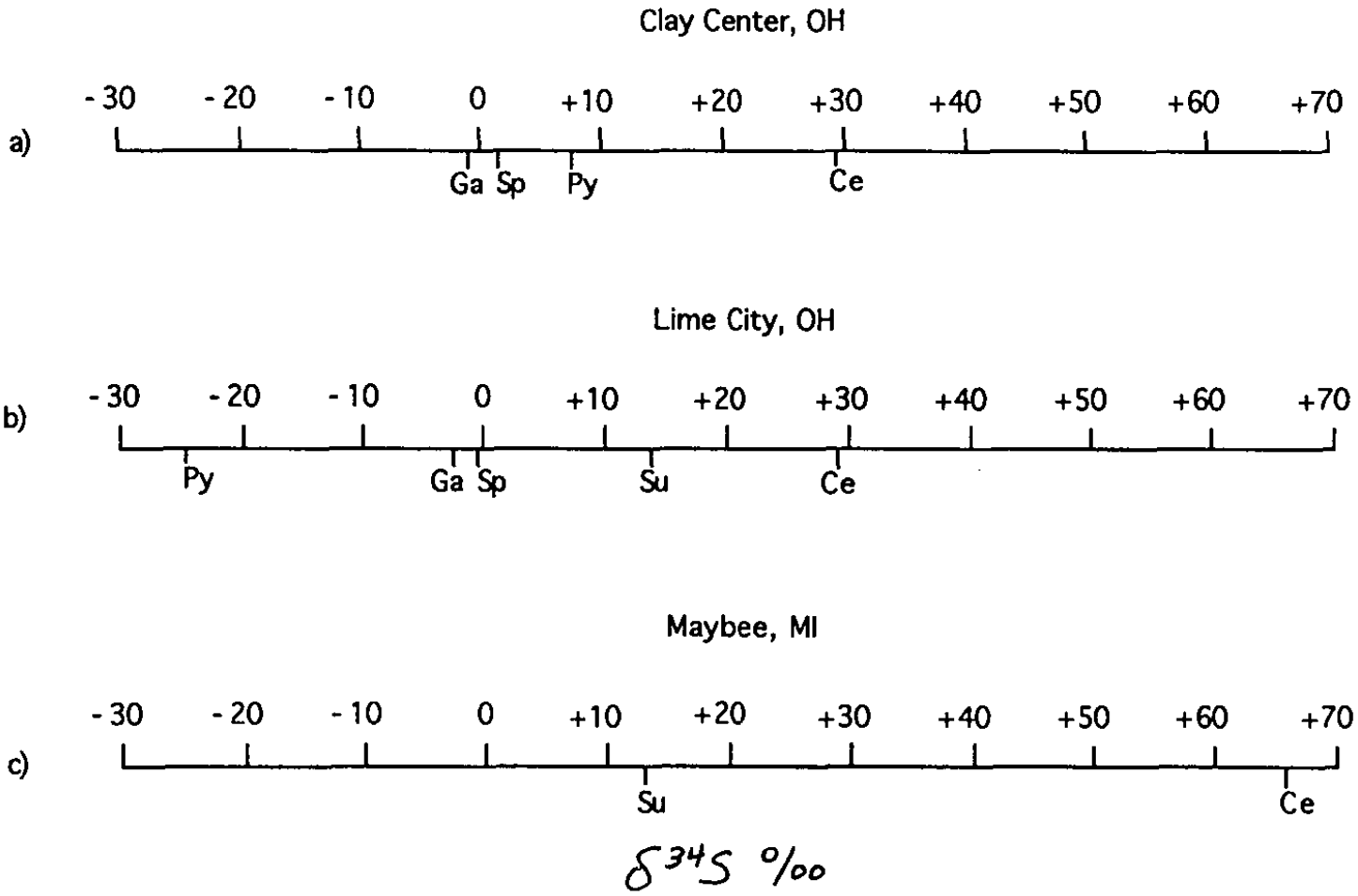


Figure 5 Sulfur isotope compositions for the quarries at a) Clay Center, b) Lime City, and c) Maybee. The numbers refer to $d^{34}S$ (in ‰) and the letters Py, Ga, Sp, Su, and Ce represent pyrite, galena, sphalerite, native sulfur, and celestite, respectively. They are placed at the corresponding $d^{34}S$ on the scale. Notice that celestite is highly enriched in ^{34}S.

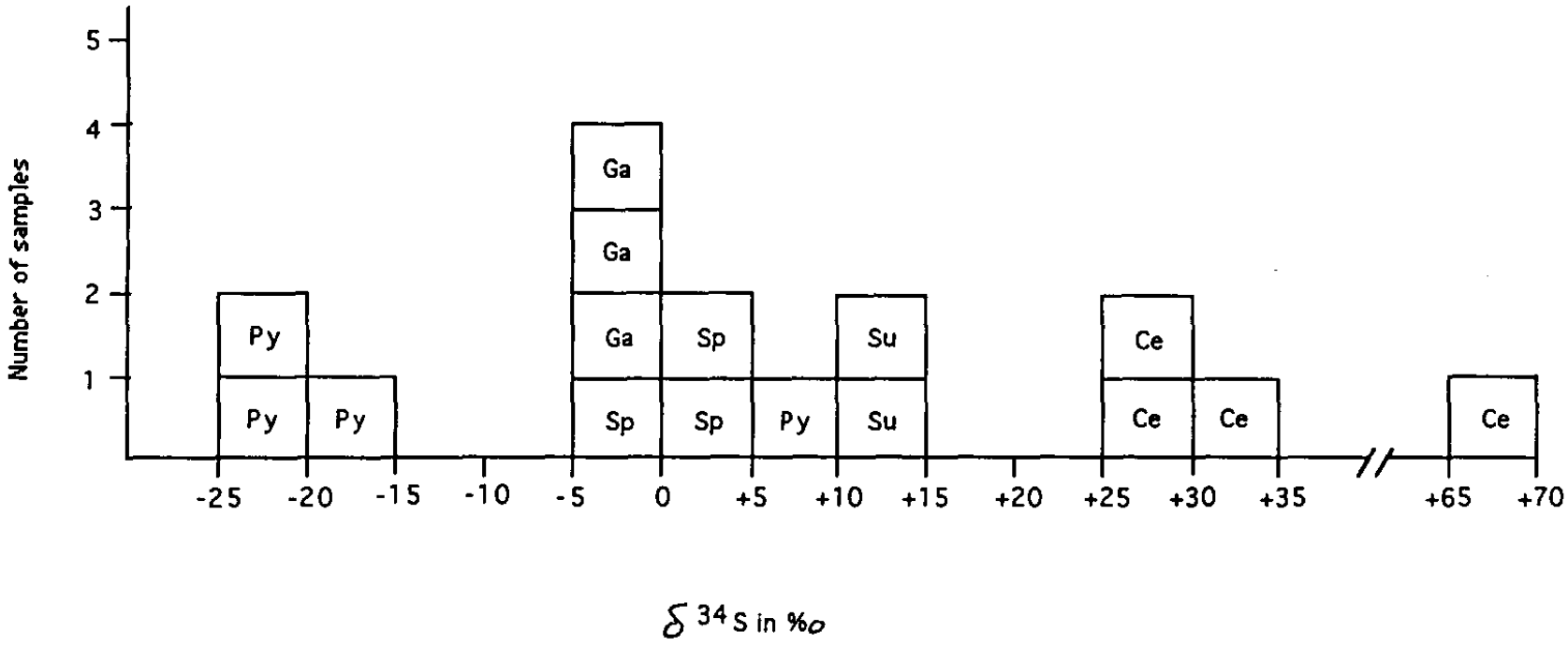


Figure 6 Histogram of $\delta^{34}S$ values for northwestern Ohio and southern Michigan. The letters Py, Ga, Sp, Su, and Ce refer to pyrite, galena, sphalerite, native sulfur, and celestite, respectively. Notice that the sulfide minerals are more depleted in ^{34}S than celestite.

Rayleigh Distillation

The differences in the isotope compositions of carbon and sulfur are explainable by means of the Rayleigh equation applied to the metabolic activity of bacteria. Rayleigh distillation occurs when there is a limited amount of sulfate and when H_2S can escape from the system by deposition as sulfide minerals (Faure, 1991). The fractionation factor (α) is the isotope ratio for any two compounds expressed by the equation:

$$\alpha = \frac{\left(\frac{^{34}S}{^{32}S}\right)_A}{\left(\frac{^{34}S}{^{32}S}\right)_B} \qquad (3)$$

The Rayleigh distillation equation uses the fractionation factor to express the isotopic composition of the remaining sulfate. As the H_2S is removed from the system, the $\delta^{34}S$ values of the remaining sulfate become increasingly positive, according to the formula:

$$\left(\frac{^{34}S}{^{32}S}\right) = \left(\frac{^{34}S}{^{32}S}\right)_o f^{(1/\alpha)-1} \qquad (4)$$

where f is the fraction of sulfate remaining in the reservoir and $(^{34}S/^{32}S)_o$ is the initial sulfur isotope ratio of the sulfate. The $^{34}S/^{32}S$ of the remaining sulfate can be expressed in terms of the δ - notation by the relation:

$$\alpha = \frac{\delta^{34}S_{(SO_4)} + 1000}{\delta^{34}S_{(SO_4)_o} + 1000} \qquad (5)$$

As the sulfate becomes increasingly enriched in ^{34}S, the sulfides also become enriched in ^{34}S. This is expressed by the equation for the sulfide isotope composition:

$$\frac{\delta^{34}S_{(H_2S)}+1000}{\delta^{34}S_{(SO_4)_o}+1000} = (1/\alpha) * f^{(1/\alpha)-1} \qquad (6)$$

As the reservoir of sulfate is depleted, the sulfate and sulfide $\delta^{34}S$ values both become more positive, reflecting an enrichment in ^{34}S.

Interpretation

Carbonates and Petroleum

The $\delta^{13}C$ values of dolomite are generally around 1.0‰, as expected for marine carbonates. One sample has a $\delta^{13}C$ value of -9.3‰, indicating that this specimen of dolomite formed from CO_2 released by the bacteria after metabolizing petroleum. The $\delta^{13}C$ of calcite generally are negative (-11.0 to -21.5‰) and lie between dolomite and petroleum $\delta^{13}C$ values. Therefore, the isotope composition of carbon establishes a genetic link between secondary calcite and petroleum, as expected if bacteria had derived the carbon from petroleum.

Sulfur Isotopes and Rayleigh Distillation

Whereas $\delta^{34}S$ values of galena and sphalerite vary only between narrow limits (+4.8 to -3.4‰), pyrite has a wide range of $\delta^{34}S$ values (+7.0 to -24.2‰). The range of sulfur isotope compositions can be accounted for by Rayleigh distillation (Figure 7), using $\delta^{34}S$ = +28‰ for the original sulfur isotope composition of marine sulfates during Silurian and Devonian time (Faure, 1986). Assuming a fractionation factor of 1.025, the sulfate isotope compositions become increasingly enriched in ^{34}S as the amount of sulfate

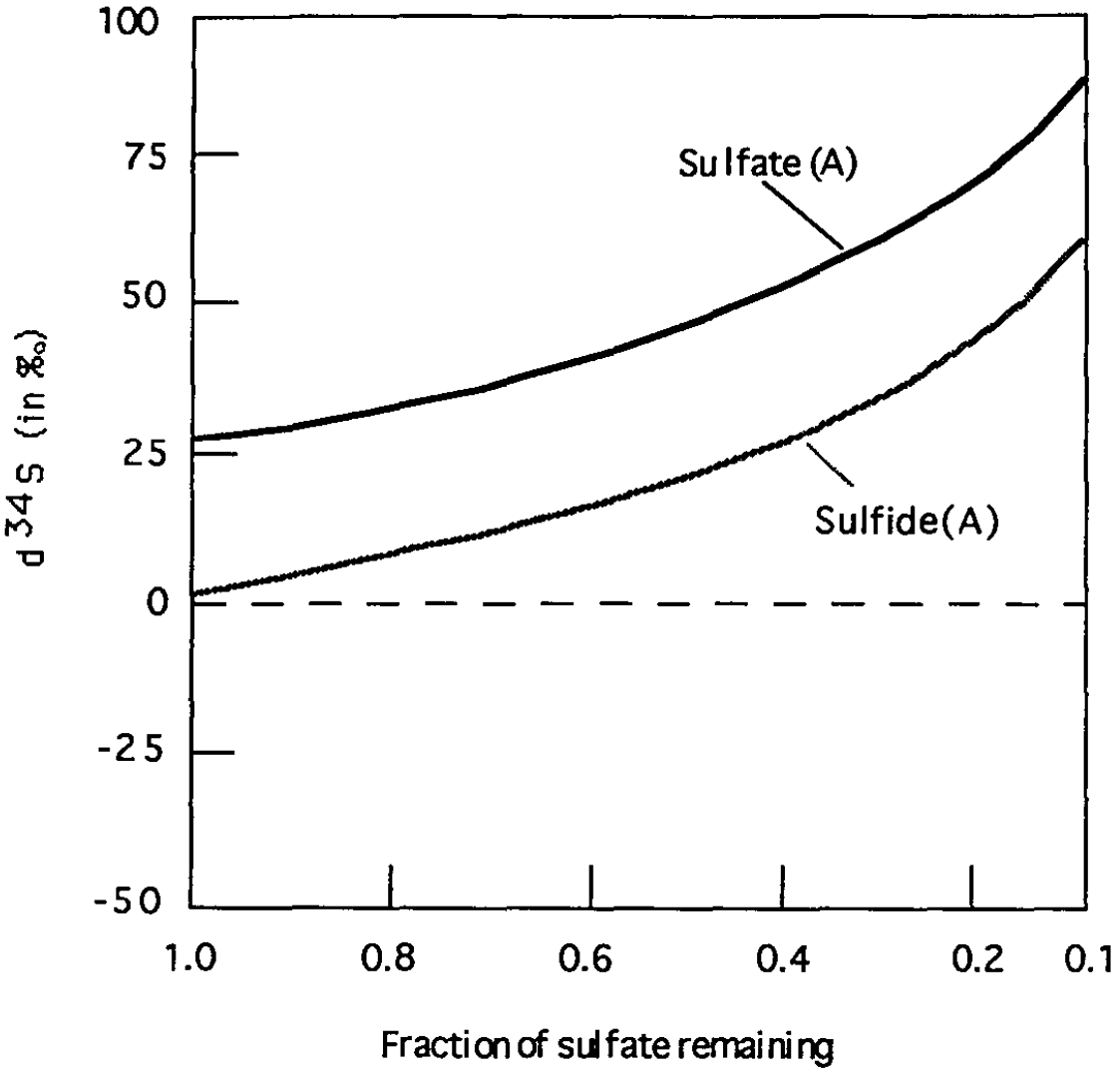


Figure 7 Rayleigh distillation showing sulfate and sulfide sulfur isotope compositions as the amount of sulfate decreases. The Sulfate(A) and Sulfide(A) curves are modeled using a fractionation factor of 1.025.

remaining in the reservoir decreases. The sulfide $\delta^{34}S$ values also become enriched in ^{34}S as shown by the sulfide(A) curve of Figure 7. However, most of the specimens of sulfide minerals in northwestern Ohio have negative $\delta^{34}S$ values. For this reason, the fractionation factor was increased to 1.05, as shown in the sulfide (B) curve of Figure 8, which causes the $\delta^{34}S$ values of the sulfide minerals to be negative, thus matching the observed isotope compositions. Nakai and Jensen (1964) reported that bacteria can produce fractionation factors from 1.043 to 1.062 when there is a limited sulfate supply. Therefore, Rayleigh distillation reproduces the observed range of isotope compositions and thereby strengthens the evidence for a bacteriological origin of secondary minerals in northern Ohio.

The Rayleigh distillation model also accounts for the highly fractionated $\delta^{34}S$ values of the sulfate in celestite. As the amount of sulfate in the reservoir decreased, the sulfate became increasingly enriched in ^{34}S, which can explain the $\delta^{34}S$ range of +28.4 to +66.4‰ of celestite. The isotope compositions of native sulfur reflect times when a lower fractionation factor was operative (such as less than 1.025), which is possible if the bacterial population decreased for some reason. Another possible explanation for the isotope composition of native sulfur is that it formed when the reservoir had been nearly depleted of sulfate, causing the sulfur to be more enriched in ^{34}S, as in the Rayleigh distillation model.

These data confirm that sulfur-reducing bacteria were involved in the deposition of secondary minerals in northwestern Ohio. Therefore, the conclusion that some of these secondary minerals were deposited by hydrothermal fluids of magmatic origin as suggested by Botoman and Faure (1976) is inaccurate. This explanation requires that the $\delta^{34}S$ remain near zero and fails to account for the wide range of sulfur isotope compositions.

A search for sulfide deposits in Ohio should concentrate on rock formations that

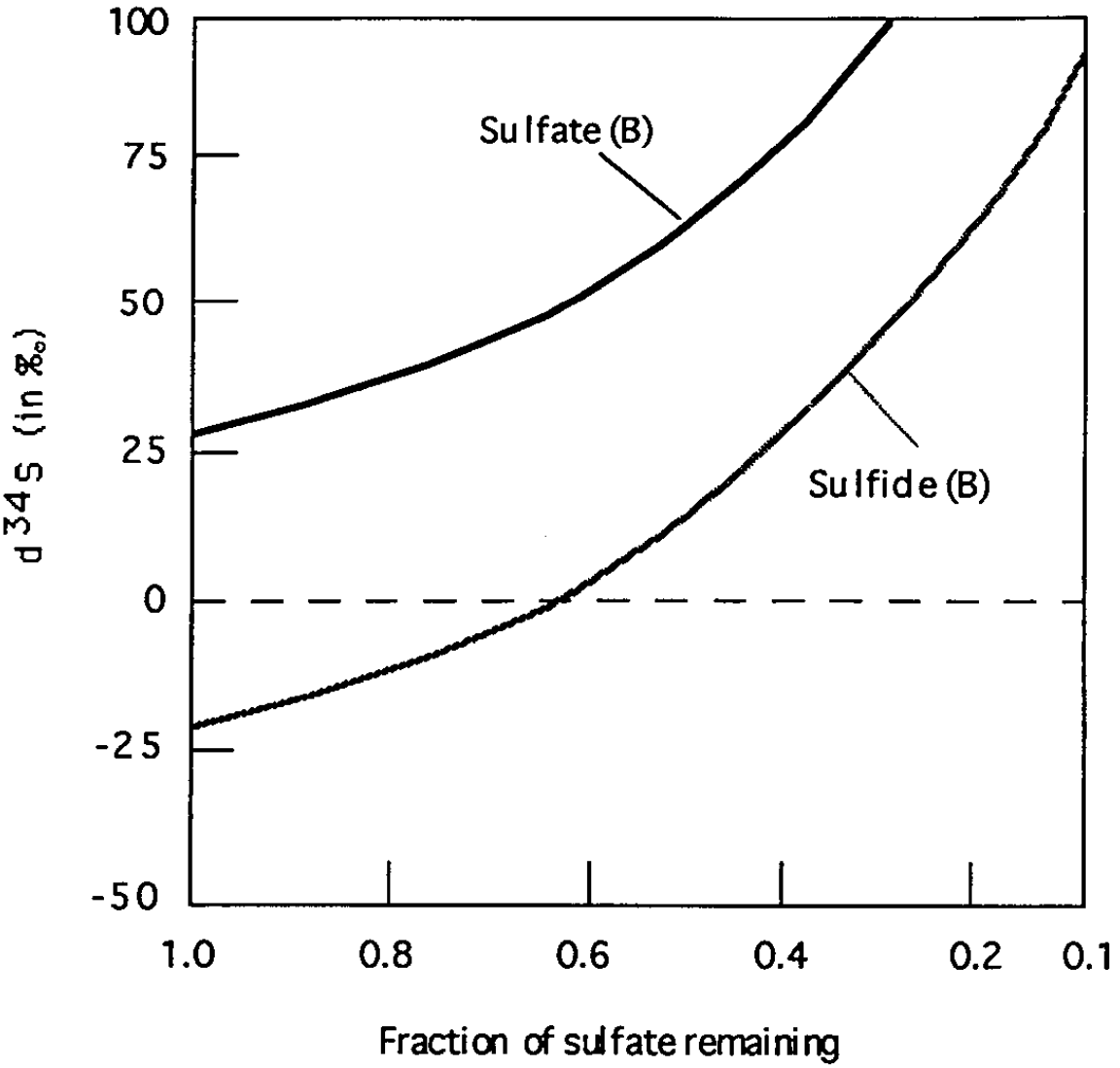


Figure 8 Rayleigh distillation showing sulfur isotope compositions with a fractionation factor of 1.05. The sulfide isotope compositions are more depleted in ^{34}S, as shown in the Sulfide (B) curve, than those of the Sulfide (A) curve of Figure 7. Therefore, the sulfide minerals from northwestern Ohio with negative $\delta^{34}S$ values would have formed in an environment with a fractionation factor similar to that of the sulfide (B) curve. The larger fractionation factor would have been possible if sulfur-reducing bacteria were involved.

contain petroleum reservoirs. If present in significant quantities, mining of galena and sphalerite can be a significant source of income for Ohio. Additionally, it may be possible to apply the findings of this study to MVT deposits in other areas.

Conclusion

The secondary calcite has negative $\delta^{13}C$ values between those of petroleum and dolomite. This relation establishes a genetic link between secondary calcite and petroleum, which occurs when bacteria metabolize the petroleum. The sulfide minerals are consistently depleted in the heavy sulfur isotope compared to coexisting sulfate minerals. Using the Rayleigh distillation equation, it is possible to demonstrate that bacteria can fractionate sulfur isotopes sufficiently to produce the $\delta^{34}S$ values found in the samples.

The isotope fractionation of carbon and sulfur in minerals of northwestern Ohio confirms that sulfur-reducing bacteria metabolized hydrocarbons by means of oxygen derived by reduction of sulfate to sulfide, resulting in the deposition of secondary carbonate and sulfide minerals. This finding also means that a search for large MVT mineral deposits would best be conducted in areas where petroleum reservoirs are (or were) present. Because sphalerite and galena are valuable ore minerals, this conclusion has important economic significance for the state of Ohio. In addition, it may be possible to apply these findings to the study of MVT deposits in other areas.

Acknowledgments

I would like to thank the Friends of Orton Hall and the Pressey Honors Endowment for their financial support of this research. I am also grateful to Dr. Faure for his continued guidance and encouragement. In addition, many thanks to Akihide Mizutani for advice on statistics, and to friends and family for their support.

References Cited

Botoman, G. and G. Faure (1976) Sulfur isotope composition of some sulfide and sulfate minerals in Ohio. *The Ohio Journal of Science*, 76 (2), 66-71.

Botoman, G. and R.D. Stieglitz (1978) The occurrence of sulfide and associated minerals in Ohio. Report of Investigations No. 104, Ohio Geological Survey, 11p.

Carlson, E.H. (1991) Minerals of Ohio, Ohio Geological Survey Bulletin 69, 155p.

Davis, J.B. and D.W. Kirkland (1970) Native Sulfur Deposition in the Castile Formation, Culberson County, Texas. *Economic Geology*, 65, 107-121

Faure, G. (1991) *Principles and Applications of Inorganic Geochemistry*, Prentice-Hall, New Jersey, 626p.

Faure, G. (1986) *Principles of Isotope Geology*, 2nd ed., John Wiley and Sons, Inc., New York, 589p.

Guilbert, J. M. and C.F. Park, Jr. (1986) *The Geology of Ore Deposits*, W.H. Freeman & Co., New York, 983p.

Haden, J. M. (1977) Isotopic Studies of Sulfide and Other Mineralization from the Middle Paleozoic Rocks of Western Ohio. Unpublished M. Sc. Thesis, Department of Geology and Mineralogy, The Ohio State University, 117p.

Heyl, A.V., G.P. Landis, and R.E. Zartman (1973) Isotopic evidence for the origin of Mississippi Valley type mineral deposits: a review. *Economic Geology*, 68, 1207

Hoefs, J. (1997) *Stable Isotope Geochemistry*, 4th ed., Springer-Verlag, New York, 201p.

Janssens, A. (1977) Silurian rocks in the subsurface of northwestern Ohio. Report of Investigations No. 100, Ohio Geological Survey, 96p.

Janssens, A. (1970) Middle Devonian formations in the subsurface of northwestern Ohio. Report of Investigations No. 78, Ohio Geological Survey, 22p.

Janssens, A. (1968) Stratigraphy of Silurian and pre-Olentangy Devonian rocks of the South Birmingham Pool area, Erie and Lorain counties, Ohio. Report of Investigations No. 70, Ohio Geological Survey, 20p.

Nakai, N. and Jensen, M.L. (1964) The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochem et Cosmochem Acta*, 28, 1893-1912

Spencer, R. J. (1987) Origin of Ca-Cl brines in Devonian formations, western Canada sedimentary basin. *Applied Geochemistry*, 2, p. 373-384,